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COMPETITION KINETICS OF
PHOTOELECTROCHEMICAL PROCESSES ON
SEMICONDUCTING IRON OXIDE ELECTRODES

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ABSTRACT

Results of photoelectrochemical measurements using semiconducting iron oxide electrodes are presented. Photocurrent was measured as function of electrode potential, solution content and illumination intensity. The dependence of photocurrent on reducing agent concentration was described in terms of a model of competition kinetics. A simple mechanism was proposed: photo-generated minority carriers, arriving at the surface are either injected into the solution or recombine. The flux of minority carriers i.e. hole flux can be determined as a parameter of the kinetic equation. It has been found that the experimentally determined hole flux as function of light intensity and electrode potential cannot be described in terms of Gärtner's depletion layer theory.

АННОТАЦИЯ

В работе описаны результаты фотоэлектрохимических измерений электродов из окиси железа. Фототок был измерен в зависимости от потенциала электродов, интенсивности освещения и состава раствора. Зависимость фототока от концентрации восстановителя описана в рамках конкурирующей кинетической модели. Дано простое предложение для механизма описания процессов, происходящих на граничной поверхности полупроводник-электрод, согласно которому выходящие под воздействием света на граничную поверхность основные носители заряда либо инжектируются в раствор, либо рекомбинируются. Ток выходящих на граничную поверхность основных носителей заряда - дыр - был определен как один из параметров конкурирующей кинетической модели, зависимость которой от потенциала электрода и от интенсивности света нельзя сравнить с относящейся к этой ситуации теорией Гертнера.

KIVONAT

Vas-oxid elektródokon végzett fotoelektrokémiai mérések eredményeit közöljük. Megmértük a fotoáramot az elektródpotenciál, a megvilágítás intenzitása és az oldatösszetétel függvényében. A fotoáramnak az oldat redukálószer-koncentrációjától való függését egy versengő kinetikai modell keretén belül írjuk le. A félvezető - elektrolit határfelületen végbemenő folyamatokra egyszerű mechanizmust javasoltunk, mely szerint a határfelületre kijutó, fény keltette kisebbségi töltéshordozók vagy oldatba injektálódnak, vagy rekombinálódnak. A határfelületre kijutó kisebbségi töltéshordozók - lyukak - árama a versengő kinetikai modell egyik paramétereként meghatározó volt, és megállapítottuk, hogy ennek sem elektródpotenciáltól, sem fényintenzitástól való függése nem egyeztethető össze Gärtner ide vonatkozó elméletével.

INTRODUCTION

Since 1972, when Fujishima and Honda [1] demonstrated the possibility of water decomposition on illuminated semiconductor electrodes, there has been considerable interest in the photoelectrochemical behaviour of semiconducting electrodes, especially n type ones. The dependence of photocurrent on various parameters is most frequently examined. These parameters are bulk and surface properties of semiconductor such as chemical composition, crystal homogeneity, texture, dopant concentration, surface orientation, surface pretreatment of the electrode substance, composition of electrolyte, electrode potential, wavelength and intensity of illumination. The examinations presented here relate to the dependence of photocurrent on electrolyte content, electrode potential and light intensity on n type iron oxide electrodes; our aim being to compare the experimental results with various theories - especially with that of Gärtner [2] and to show, how these models are modified if surface processes are taken into account.

The difference between photocurrent j_p , and dark current j_d , which is called excess photocurrent j' , can be treated in the simplest case by Gärtner's depletion layer theory [2]. This theory describes the flux of minority carriers in terms of potential drop in the semiconductor space charge layer, of light intensity and of some physical properties of the semiconductor. Using the theory for band gap illuminated reverse biased semiconductor - electrolyte junctions, the potential drop in the semiconductor's depletion layer is

$$U_{sc} = \varepsilon - \varepsilon_{fb}$$

and

$$j' = c_1 I (1 - c_2 \exp(-c_3 \sqrt{|U_{sc}|})) \quad /1/$$

where U_{sc} is the potential drop in the depletion layer;

ϵ the electrode potential;

ϵ_{fb} the flat band potential;

I the intensity of illumination, and

c_1, c_2, c_3 are constants for a given semiconductor

and wavelength of illumination. The constants contain bulk properties of semiconductor: light absorbance, diffusion length of minority carriers, dopant concentration and permittivity. In the case of an n type semiconductor, whose electrode potential is more positive than the flat band potential, band gap illumination causes anodic excess photocurrent, being proportional to light intensity and increasing with increasing electrode potential. There is a very important condition used for the deduction of eq. [1], viz. that the photogenerated minority carriers /holes in n type semiconductors/ reaching the interface are injected into the solution with unit probability; this means that the interface is a perfect sink for them. Despite the fact that in some cases the applicability of the theory has been verified [3-5], that the measured polarisation curve can be fitted to eq [1] and that usually the trends of the measured photopolarization curves agree well with the model, it seems that this is an over-simplified model for describing all photoelectrochemical measurements. Some experiments have shown that surface processes are to be taken into account, so the assumption of the Gärtner theory /that the interface is a perfect sink for minority carriers/ is not always valid for such electrochemical systems. The experiments to be found in the literature are:

a/ Excess photocurrent depends on the pretreatment of the semiconductor surface [6,7];

b/ On some semiconductors the presence of certain solutes caused enhancement of photocurrent [5,8,9]. These experiments pointed to the importance of surface processes, i.e. surface recombination and injection of minority carriers into the solution. The consequence of surface processes is that if minority carriers arriving at the surface do not get injected into the solution instantaneously, they accumulate and recombine there. It is highly likely that different surface pretreatment alters the surface recombination rate, and that a change in the concentration of reducing agents /hole acceptors/ or oxidizing agents /electron acceptors/ causes a change in the injection rate, and thus in the excess photocurrent.

Certain theories [10-16] have been developed recently taking into account a large number of processes occurring at the semiconductor - electrolyte interface. These theories, however, are not easy to check because the large number of free parameters. Instead of using these theories we singled out the idea of competition between minority carrier injection and recombination at the and these single processes are supposed to play a decisive role. On this basis a simplified, phenomenological kinetic description will be given here. We wish to examine the existence experimentally of this competition and to clarify the factors which possibly influence the rate of processes. In order to investigate competition between recombination and injection, iron oxide photoelectrodes were studied. Judging by the publications that have

appeared recently, iron oxide electrodes showed stability against photocorrosion, the semiconductor has a band gap of about 2 eV; this means that it is a practical candidate for solar cell photoelectrodes.

Different types of electrodes were examined: besides single crystalline hematite [17-19] oxide layers produced by RF sputtering [19], or by CVD [21,22], were investigated. A number of studies were carried out also on thermally grown oxides [9,19,20,23,24].

All the reported photoelectrodes behaved as n type semiconductors except the RF sputtered ones in Ref. [19]. In the case of electrode potentials more anodic than the flat band potential, the anodic photocurrent can be measured on n type electrodes, when illuminated by light of wavelength shorter than about 600 nm, in accordance with the band gap of hematite. The flat band potential of the electrodes determined from the intercept of a Mott-Schottky plot, is around +0.4 V against hydrogen electrode in the same solution. ϵ_{fb} depends on the acidity of the solution, the shift is around -60 mV/pH /except in the findings in Ref. [20]/. In some cases photocurrent enhancement was observed viz. when the electrolyte contained sodium citrate or EDTA [5] or H_2O_2 [9]. In the former case the effect was interpreted as being the result of interaction of the oxide surface with complexing ions.

Because we wished to examine charge transfer at the illuminated semiconductor interface and to compare the experimental results with the phenomenological model of competition, photocurrents were measured on iron oxide electrodes as a function of electrode potential, solution content and light intensity. We interpreted the measured data by means of a simple phenomenological model, containing competition of recombination and hole injection. The parameters of the model were examined to see whether they depended on electrode potential and light intensity.

PHENOMENOLOGICAL MODEL OF HOLE INJECTION AND RECOMBINATION AT THE SURFACE OF THE SEMICONDUCTOR

We deduce the rate equation expressing competition minority carrier injection and recombination. Without loss of generality in the following parts only n type semiconductors will be considered, i.e. the minority carriers are holes. Under band gap illumination j^x a flux of photogenerated holes arrive at the surface, where the holes are either injected into the solution or recombine with majority carriers. The hole flux j^x is supposed to depend only on electrode potential and light intensity and is independent of surface processes. In the steady state the number of arriving holes equals the sum of recombining and injected holes, thus

$$j^x = j_r + j_i \quad /2/$$

where subscripts r and i denote recombination and injection, respectively, and j^x is the current density of holes.

Let the rate of hole injection as well as that of recombination be considered to be proportional to hole concentration at the surface, and let the former rate be proportional to the surface concentration of hole acceptors of the solution. Furthermore let us suppose that in the solution there is only one kind of reducing ions or molecules. Then eq. /2/ in the steady state is of the form:

$$j^x = k_r p + k_i c_{red}^s p \quad /3/$$

where p is the hole density at the surface of the semiconductor,

c_{red}^s concentration of the reducing substance in the solution at the surface

k_r and k_i are rate constants of recombination and injection, respectively.

Hence

$$p = \frac{j^x}{k_r + k_i c_{red}^s} \quad /4/$$

and since

$$j' = j_i = k_i c_{red}^s p$$

$$j' = j^x \frac{k_i c_{red}^s}{k_r + k_i c_{red}^s} \quad /5/$$

or

$$\frac{1}{j'} = \frac{1}{j^x} \left(1 + \frac{k_r}{k_i c_{red}^s} \right) \quad /5a/$$

This equation gives a direct relation between excess photocurrent and concentration of reducing agents. If there is more than one type of hole acceptors in the solution, we have to take into account competition among them. For example, if hole injection into solvent and reducing ions occurs simultaneously, the following equation holds,

$$\frac{1}{j' - j'_b} = \frac{1}{j^x - j'_b} \left(1 + \frac{k_r}{k_i c_{red}^s} \frac{j^x}{j^x - j'_b} \right) \quad /5b/$$

where $j'_b = k_{i,b} p$ is the flux of holes injecting into the solution being free of reducing agents. The rate constant of this process is $k_{i,b}$.

If the hole injection rate constant is sufficiently large, such as to make the transport of hole acceptors be the rate determining step, then eq. /5/ needs to be modified. In this case, under steady state conditions, the rate of hole injection is equal to that of diffusion of hole acceptors, that is,

$$j_i = k_i c_{\text{red}}^s p = X(c_{\text{red}}^b - c_{\text{red}}^s) \quad /6/$$

where c_{red}^b denotes the bulk concentration of hole acceptors, and X is the rate constant of the transport process of hole acceptors in the solution. On a rotating disc electrode /RDE/ [21]

$$X = A\omega^{+1/2} \quad /7/$$

where $2\pi\omega$ is the angular velocity of RDE, and A is constant in a given solution. It should be stressed, however, that eq. /7/ is not valid for very low angular velocities. This is so because spontaneous convections mix always the liquid. That makes $X(\omega=0)$ assume a non zero, indefinite value.

From eqs. /2/, /5a/, /6/ and /7/ one finds:

$$\frac{1}{j'} = \frac{1}{j^x} \left(1 + \frac{k_r}{k_i c_{\text{red}}^s} + \frac{(j^x - j')}{A c_{\text{red}}^b \sqrt{\omega}} \right) \quad /8/$$

If the transport rate is large enough, the last term in the expression approaches zero, c_{red}^s approaches c_{red}^b , so eq. /5a/ is recovered.

EXPERIMENTAL

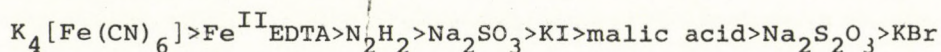
Iron oxide photoelectrodes were made a similar way to that described by Yeh et al. [23]. Spectral grade iron discs of 10 mm diameter were polished, degreased and heated in a furnace for an hour at 550 C°. After heating the discs were slowly cooled. The rear side of the discs were polished and soldered to brass rods of the same diameter. The metallic parts of the discs and the brass rods were insulated by layers of laquer or by epoxy resin. As scanning electron micrographs showed, the surface of the oxide was quite rough, there were crystal faces of 1-100 μm seen, but no pores were observable. The electrochemical measurements were carried out in the usual way; a 100 cm³ flat bottomed cell was used with SCE reference. The working electrode with the brass rod was fixed to the shaft of a stirrer motor, so the iron oxide electrodes could be used as RDE. Electrolyte solutions were deaerated by means of bubbling high purity nitrogen before and during the measurements. An operational amplifier potentiostat was used, in some cases IR compensation was applied. In certain experiments photocurrent transients were observed by oscilloscope, the fast switching on of the illumination having been achieved by means of a rotating sector. Electrolyte solutions were borate buffers of pH 9,0 in which analytical grade reducing substances were dissolved. The pH of these solutions was re-established by the addition of acidic or alkaline solutions when it was found to be necessary. Illumination of the electrodes was carried out by means of 150 W halogen lamps, fed from a stabilized DC

power supply. A series of densely woven metal sieves was utilized as a variable neutral density filter. In those measurements, when coloured substances were dissolved in the electrolyte /e.g. $K_4[Fe(CN)_6]$ / the distance between the electrode and the cell window was altered, so that the product of the light path and concentration of the absorbing species remained constant, according to Beer's law.

The reproducibility of measured photocurrents in short time intervals was found to be acceptable, ageing effects causing about 5% drift in photocurrent per day at medium potentials $+0.3 \text{ V} < \epsilon - \epsilon_{fb} < +0.9 \text{ V}$ and under strong illumination. Taking into account ageing of the electrodes, the time of a measurement series had to be shorter than four hours. During this time, our results show better than 2% reproducibility on one and the same sample. The scatter between different samples was much larger, so only measurements carried out on one and the same samples were directly compared.

RESULTS

Judging by our measurements the photocurrent on the iron oxide electrodes is greatly influenced by the nature and concentration of the reducing substances in solution. The excess photocurrent increases with increasing concentration of the reducing substance, but the dark current does not change unless the electrode potential is very anodic $[\epsilon - \epsilon_{fb} < 1.2 \text{ V}]$. The dependence of photo - and of dark currents on the electrode potential in electrolytes with and without Na_2SO_3 is shown in Fig. 1. It seems that there is a potential interval $[-0.1 - +0.5 \text{ V against SCE}]$ in which the photocurrent in the supporting electrolyte is negligible compared to with that in the solution of the reducing substance, so in this interval the excess photocurrent can safely be attributed to the oxidation of Na_2SO_3 . Measurements concerning the relationship between excess photocurrent and concentration of the reducing agent was carried out in this potential interval, which made j'_b in eq. /5b/ negligible. The excess photocurrent was increased by addition of the following reducing substances; their effect decreasing in the sequence:



The first several substances may be called as effective or fast hole acceptors, the latter ones ineffective or slow ones. The photocurrent was influenced by stirring the dilute solutions of the first substances at high light intensity. In these cases the rotating disc electrode technique was applied as is shown later. The relationship between excess photocurrent and concentration of reducing agent corresponds to eq. /5a/, /Fig. 2/. The reciprocal of the intersect is j^x which is the total hole flux to the surface of the semiconductor. From the slope and intersect the ratio of rate constants is obtained. The ordinate intersect must not depend on the nature of the reducing agent because the number of holes arriving at the surface is independent of the

nature of hole acceptors in the solution. This is shown in Fig. 2; the intersect is the same in solution of three different substances. It is worthy to note that the intersect does not depend on the number of elementary charges which are involved in oxidation process. The ratio of rate constants k_r/k_i depends on the nature of the reducing substance, its typical value being in the order of magnitude of 10^{-3} mol/dm³ for Na₂SO₃ and 10^{-4} mol/dm³ for K₄[Fe(CN)₆]. This means that the number of holes injected into the solution equals the number of recombining ones if the concentration of Na₂SO₃ is 10^{-3} mol/dm³. The photocurrent measured in the solution of fast reducing agents depends on stirring, thus the excess photocurrent was measured on RDE at constant potential as a function of hole acceptor concentration and rotating frequency. The measured excess photocurrent values were treated in the following manner:

The parameter j^x was fitted by trial and error, and according to eq. /8/, $1/j'$ was plotted against $(j^x - j')f^{-1/2}c_{red}^{b-1}$ /Fig. 3/. Parallel lines were obtained, and their intersects were plotted against c_{red}^{b-1} in Fig. 4. The straight line is in agreement with eq. /5a/. From this plot j^x was evaluated again. This can be regarded as a test for j^x to be correct.

According to eqs. /6/ and /8/, diffusion control has to be taken into account when $k_i p$ is large. Since p is determined by eq. /4/, the measured value of j' strongly depends on rotation frequency of the RDE if k_i and j^x is large and c_{red}^s is small. Our measurements are in agreement with the theory: diffusion control occurs when illumination is large, and there is a fast reducing substance of small concentration in the solution. The effect of stirring does not depend strongly on electrode potential in the interval of +0.4 - 1 V against flat band potential.

The potential dependence of k_r/k_i was determined and is shown in Fig. 5. k_r/k_i as a function of light intensity was also examined. As is shown in Fig. 6, an increase of one order of magnitude of illumination level increased the value of k_r/k_i by a factor of 2.

j^x depends on light intensity nonlinearly. A j^x/I against I plot is shown in Fig. 7. The height of the current peak which can be observed just after illumination /usually within 1 ms/ was also measured by making use of a rotating sector. The current transients have the shape shown in Fig. 8. The height of the transients immediately upon illumination was found to be strictly proportional to light intensity.

One of the $j^x(\epsilon)$ curves can be seen in Fig. 8. In the same figure one can see the tendency that the $j'(\epsilon)$ curves become more concave with increasing concentration of the reducing substance. The $j^x(\epsilon)$ curves are generally of concave shape, however each curve measured by us has a convex portion.

DISCUSSION

Our experimental results concerning the dependence of j' on c_{red}^s shown above correspond to eq. /5/. However, an investigation is to be carried out to see, whether some other simple mechanisms lead to similar kinetics. Equations of the same form as eq. /5a/ can be obtained if adsorption of the reducing ions is considered.

a./ Let us first neglect competition between recombination and injection and let the rate of hole injection be assumed to be proportional to the surface concentration of holes and to the coverage of the reducing substance, θ . The latter is thought to be determined by a Langmuir type adsorption isotherm, thus

$$\theta = \frac{c_{red}^b}{a + c_{red}^b} \quad /9/$$

where a is constant.

Hence for $j' = k_i \theta p$ one gets

$$\frac{1}{j'} = \frac{1}{k_i p} + \frac{a}{k_i p c_{red}^b} \quad /10/$$

In this case there is a linear relationship between $1/j'$ and $1/c_{red}^b$ as required, but the intercept is unlikely to be the same for each reducing substance.

b./ If both adsorption and competition between injection and recombination is supposed, one finds the following expression from eqs. /5/ and /9/:

$$\frac{1}{j'} = \frac{1}{j^x} \left(1 + \frac{k_r}{k_i} + \frac{a k_r}{k_i c_{red}^b} \right) \quad /11/$$

Also in this case the intercept is different for each reducing substance, because, in general, injection rate constants are expected to change from substance to substance.

Other similarly simple mechanisms, leading to similar equations were not found.

Our aim is to decide whether the surface processes can be treated in terms of simple competition kinetics. Our experiments show that it is possible. From the dependence of j' on c_{red} the hole flux to the surface can be obtained which in the simplest case can be compared with the results of the Gärtner model. According to eq. /1/, j^x should have been proportional to the illumination intensity and its dependence on electrode potential should correspond to eq. /1/. On the basis of our $j^x(\epsilon)$ measurements carried out by means of polychromatic illumination we can conclude that the Gärtner formula /eq. /1// is not applicable, i.e. this formula predicts concave curves for any wavelength; thus for polychromatic illumination too. In our measurements convex portions of the $j^x(\epsilon)$ curves were found also. The nonlinear behaviour of j^x

against light intensity also contradicts the Gärtner theory. The discrepancy is attributed to a slow process taking place at the interface. This can be explained as follows:

The peak height of the photocurrent transient of about 1 ms duration was observed to be proportional to light intensity. It was calculated [16], that the rise time of hole current is much shorter than 1 ms. The hole current is determined basically by light absorption and by charge transport, processes which are obviously independent of light intensity at our low illumination levels. Nonlinearity is observed only in the steady state in our experiments, so it is attributed to a slow process.

In our opinion nonlinearity and other discrepancies between experimental results and Gärtner theory are due to a change in the potential distribution in the interfacial region during illumination. Our work is being continued in this direction.

SUMMARY

The phenomenological description is given of processes which take place on illuminated iron oxide- aqueous electrolyte interface. The aim of this work is to describe charge transfer at the interface in terms of a simple phenomenological competition model. To this end photocurrent was measured as a function of electrode potential, illumination intensity and reducing agent concentration. The measurements have led us to the following conclusions:

- 1./ The kinetics of charge transfer at the semiconductor-electrolyte interface can be formulated as a competition between hole injection and recombination.
- 2./ The hole flux to the surface can be determined from the dependence of photocurrent on reducing agent concentration.
- 3./ The hole flux as a function of electrode potential and light intensity cannot be adequately described in terms of the Gärtner theory.

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REFERENCES

- [1] A. Fujishima, K. Honda, *Nature* 238, 37 /1972/
- [2] W.W. Gärtner, *Phys. Rev.* 116, 84 /1959/
- [3] Z.A. Rotenberg, T.V. Djavrishvili, Yu.V. Pleskov, A.I. Asatiani, *Elektrokhimiya* 13, 1803 /1977/
- [4] M.A. Butler, *J. Appl. Phys.* 48, 1914 /1977/
- [5] J.H. Kennedy, K.W. Frese, *J. Electrochem. Soc.*, 125, 709 /1978/
- [6] R.H. Wilson, L.A. Harris, M.E. Gerstner, *J. Electrochem. Soc.* 126, 844 /1979/
- [7] R.L. Van Meirhaeghe, F. Cardon, W.P. Gomes, *Ber. Bunsenges. Phys. Chem.* 83, 236 /1979/
- [8] K. Hirano, A.J. Bard, *J. Electrochem. Soc.* 127, 1056 /1980/
- [9] A.F. Sammels, P.G.P. Ang, *J. Electrochem. Soc.* 126, 1831 /1979/
- [10] J.O'M. Bockris, K. Uosaki, *J. Electrochem. Soc.* 125, 223 /1978/
- [11] H. Reiss, *J. Electrochem. Soc.* 125, 937 /1978/
- [12] R.H. Wilson, in "Semiconductor - Liquid Junction Solar Cells" pp. 67-83. Ed. A. Heller, The Electrochemical Society, Princeton New Jersey, 1977
- [13] D. Laser, A.J. Bard, *J. Electrochem. Soc.* 123, 1828 /1976/
- [14] D. Laser, A.J. Bard, *J. Electrochem. Soc.* 123, 1833 /1976/
- [15] D. Laser, A.J. Bard, *J. Electrochem. Soc.* 123, 1837 /1976/
- [16] D. Laser, *J. Electrochem. Soc.* 126, 1011 /1979/
- [17] R.K. Quinn, R.D. Nasby, R.J. Baughman, *Mat. Res. Bull.* 11, 1011 /1976/
- [18] H.H. Kung, K.S. Jarrett, A.W. Sleight, A. Ferretti, *J. Appl. Phys.* 48, 2463 /1977/
- [19] A.M. Redon, J. Vigneron, R. Heindl, G. Sella, C. Martin, J.P. Dalbera, *Solar Cells* 3, 179 /1981/
- [20] J.S. Curran, W. Gissler, *J. Electrochem. Soc.* 126, 56 /1979/
- [21] K.L. Hardee, A.J. Bard, *J. Electrochem. Soc.* 123, 1024 /1976/
- [22] K.L. Hardee, A.J. Bard, *J. Electrochem. Soc.* 124, 215 /1977/
- [23] L.R. Yeh, N. Hackerman, *J. Electrochem. Soc.* 124, 833 /1977/
- [24] T. Pajkossy, I. Molnár, M. Pálffy, R. Schiller, *Acta Chim. Acad. Scient. Hung.* 101, 93 /1979/
- [25] E. Yeager, J. Kuta, in "Physical Chemistry", Vol. IXA, Eds. H. Eyring, D. Henderson, W. Jost, p. 345. Academic Press, New York, 1970

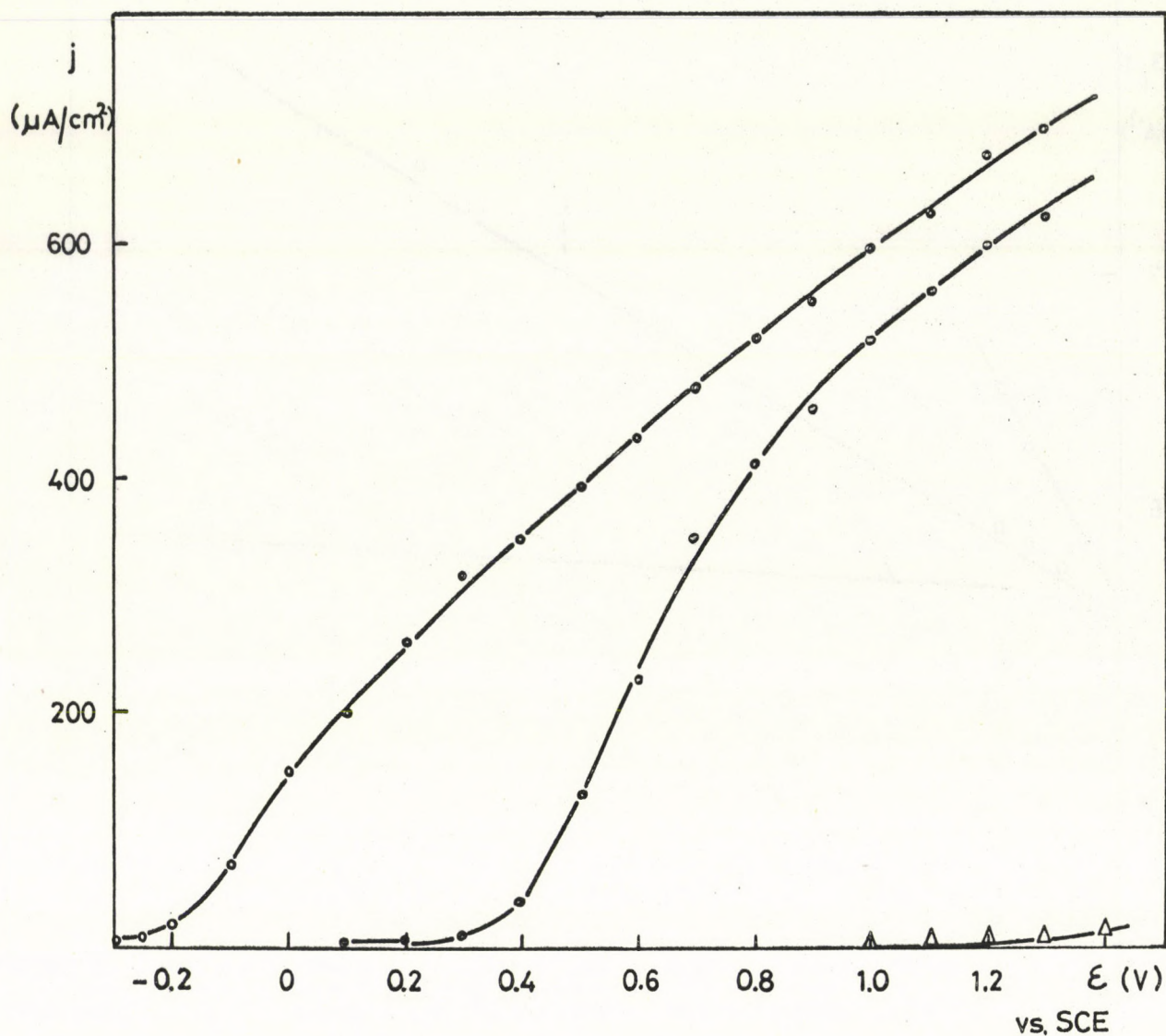


Fig. 1. Dark and photocurrents as a function of electrode potential.
 Δ dark current in borate buffer of pH 9.0
 \bullet photocurrent in borate buffer of pH 9.0
 \circ photocurrent in borate buffer of pH 9.0 containing
 0.05 M Na_2SO_3

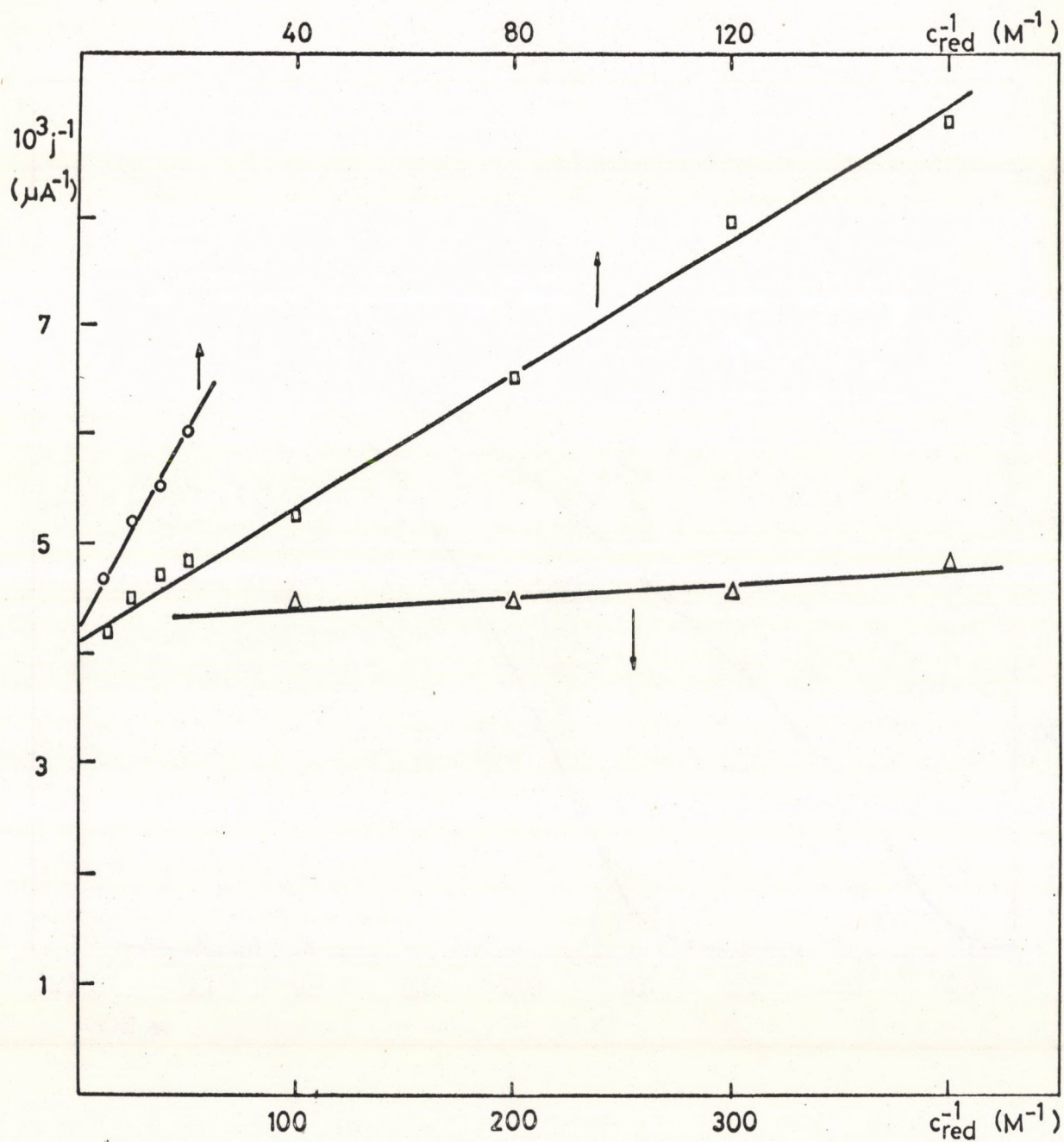


Fig. 2. Relationship between excess photocurrent and concentration of different reducing substances.
 $\epsilon = +0.2$ V vs. SCE in borate buffer of pH 9.0
 \square - Na_2SO_3 \circ - KI Δ - $K_4Fe(CN)_6$

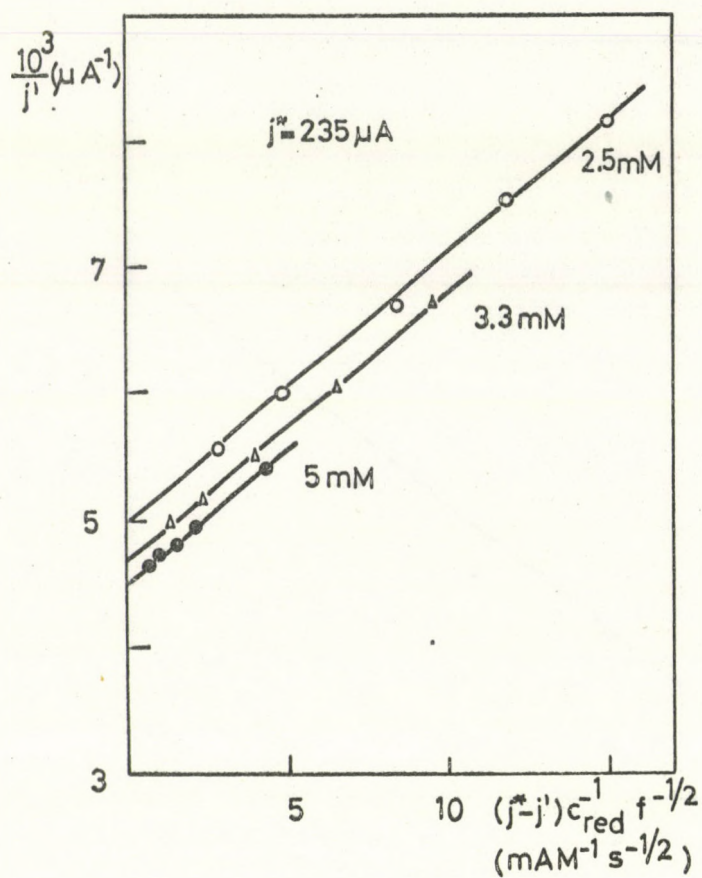


Fig. 3. Effect of electrode rotation (see text)
 $\epsilon = 0.2$ V vs. SCE in borate buffer of pH 9.0 containing
 $K_4[Fe(CN)_6]$ $j^* = 235 \mu A$ Compare with eq. /8/

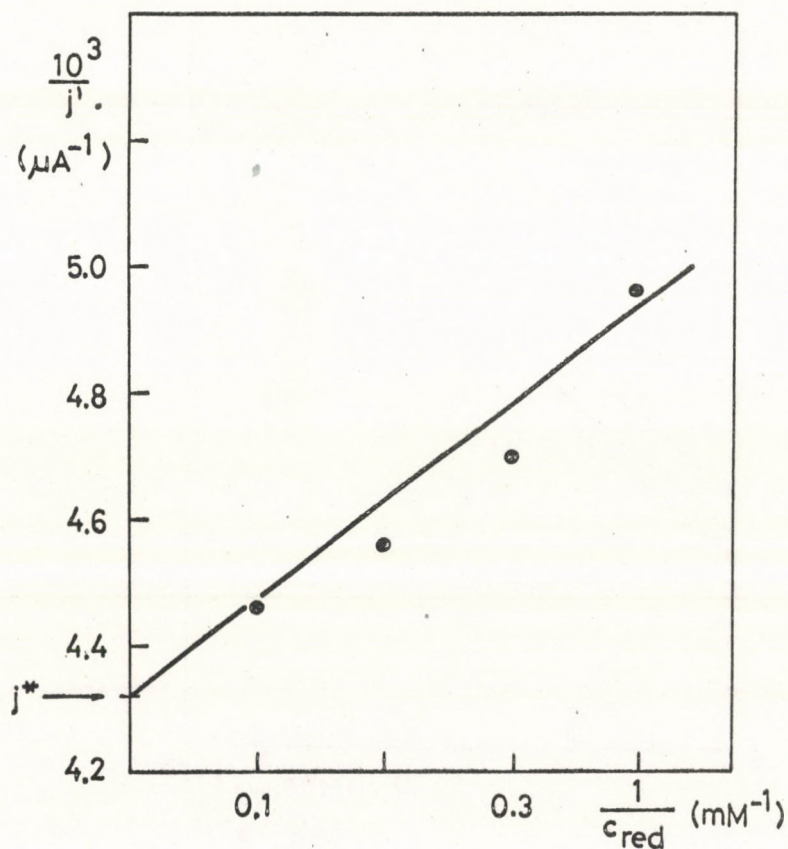


Fig. 4. Relationship between excess photocurrent and concentration of reducing substance after correction for diffusion control. For conditions, see Fig. 3. The role of diffusion in solutions of 10 mM $K_4[Fe(CN)_6]$ is not important, so this point is drawn in this figure only and not in Fig. 3.

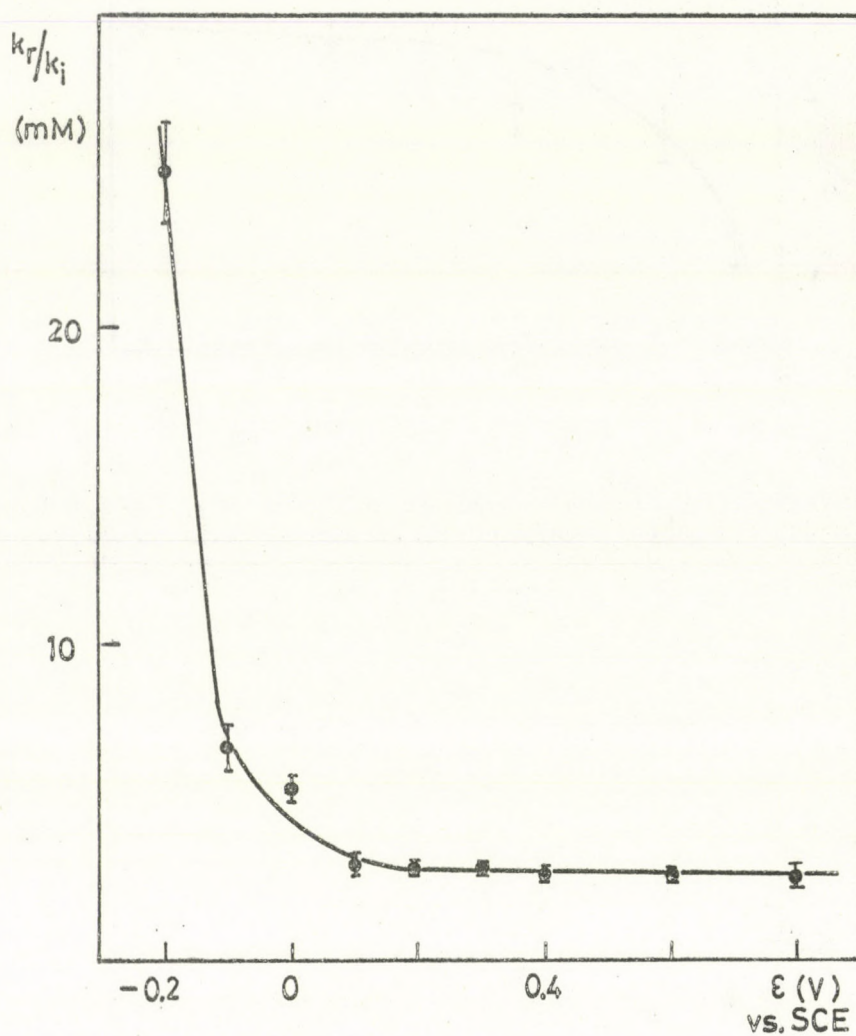


Fig. 5. Dependence of k_r/k_i on electrode potential. Determined in borate buffers of pH 9.0 containing Na_2SO_3 of various concentrations. For the evaluation of k_r/k_i eq. ²/5B/ was applied.

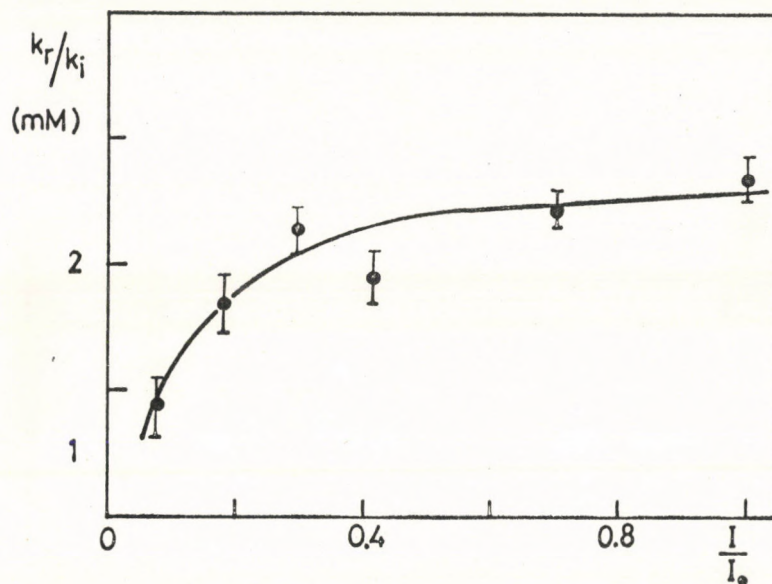


Fig. 6. Dependence of k_r/k_i on illumination intensity. $\epsilon = +0.2$ V vs. SCE. Determined in borate buffers of pH 9.0 containing Na_2SO_3 of various concentrations. I_0 is the light intensity without attenuation.

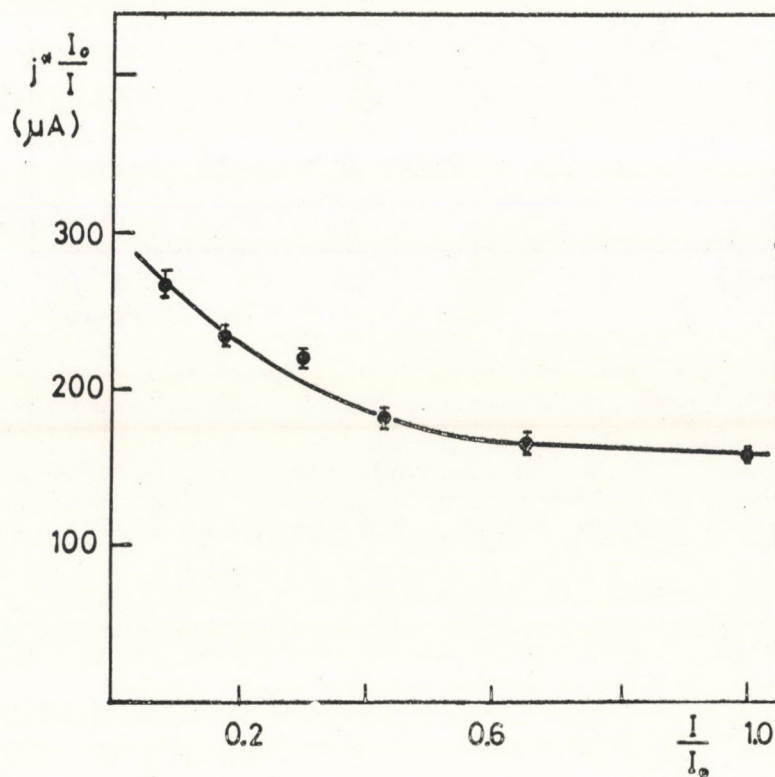


Fig. 7. Dependence of j^w/I on light intensity. For conditions see Fig. 6.

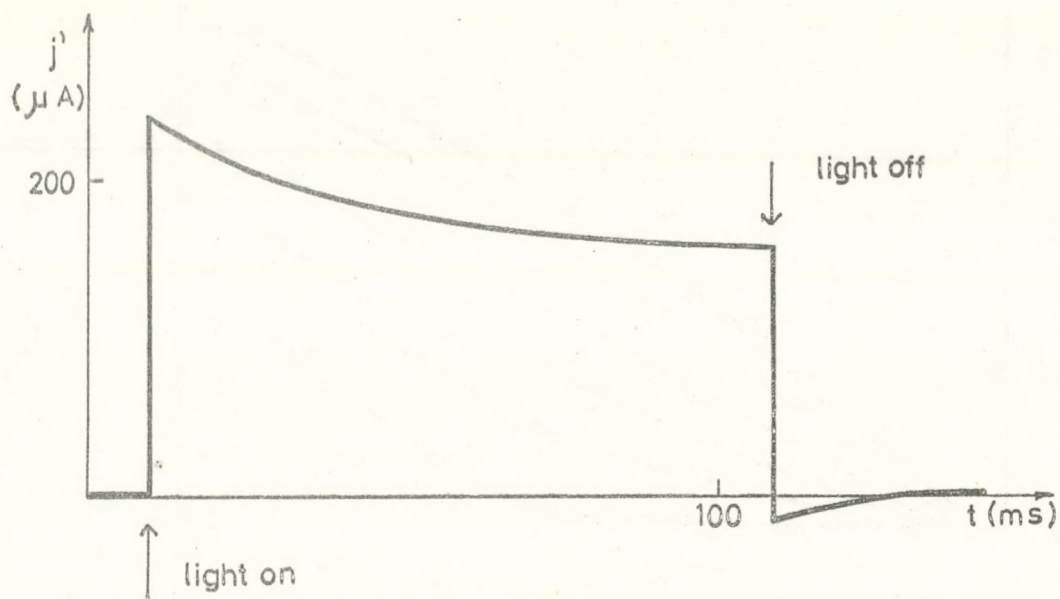


Fig. 8. Time dependence of photocurrents at medium potentials.
 $E = +0.2$ V vs. SCE in borate buffer of pH 9.0 containing
0.1 M Na_2SO_3

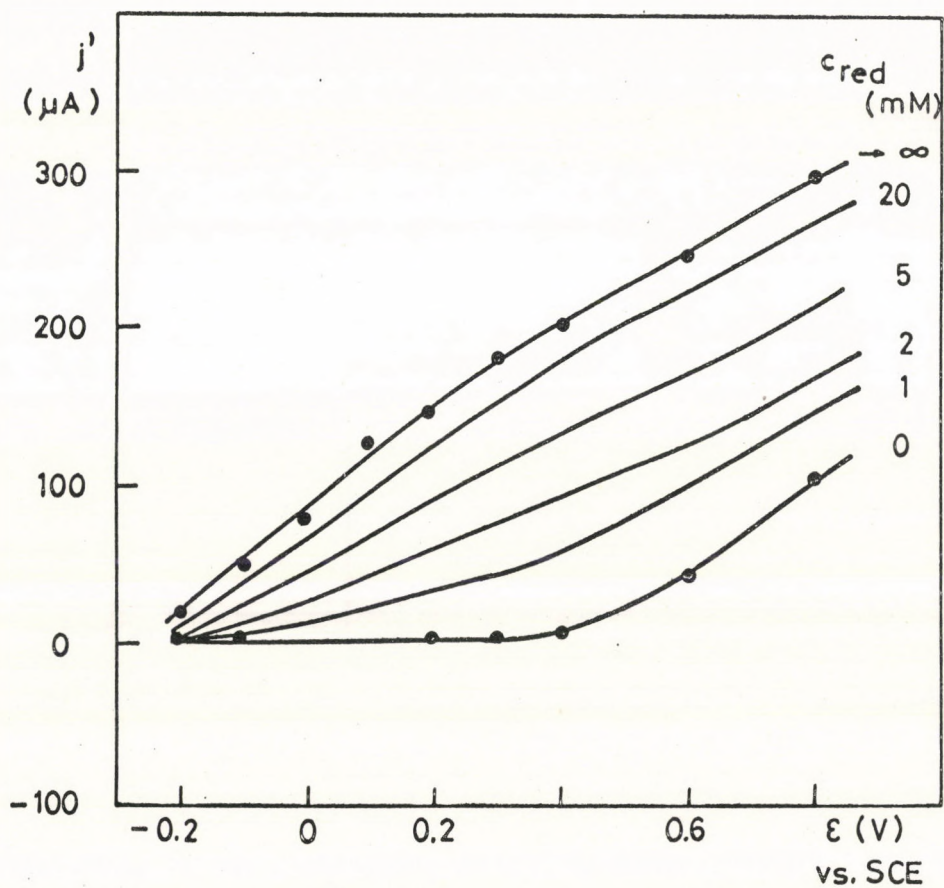
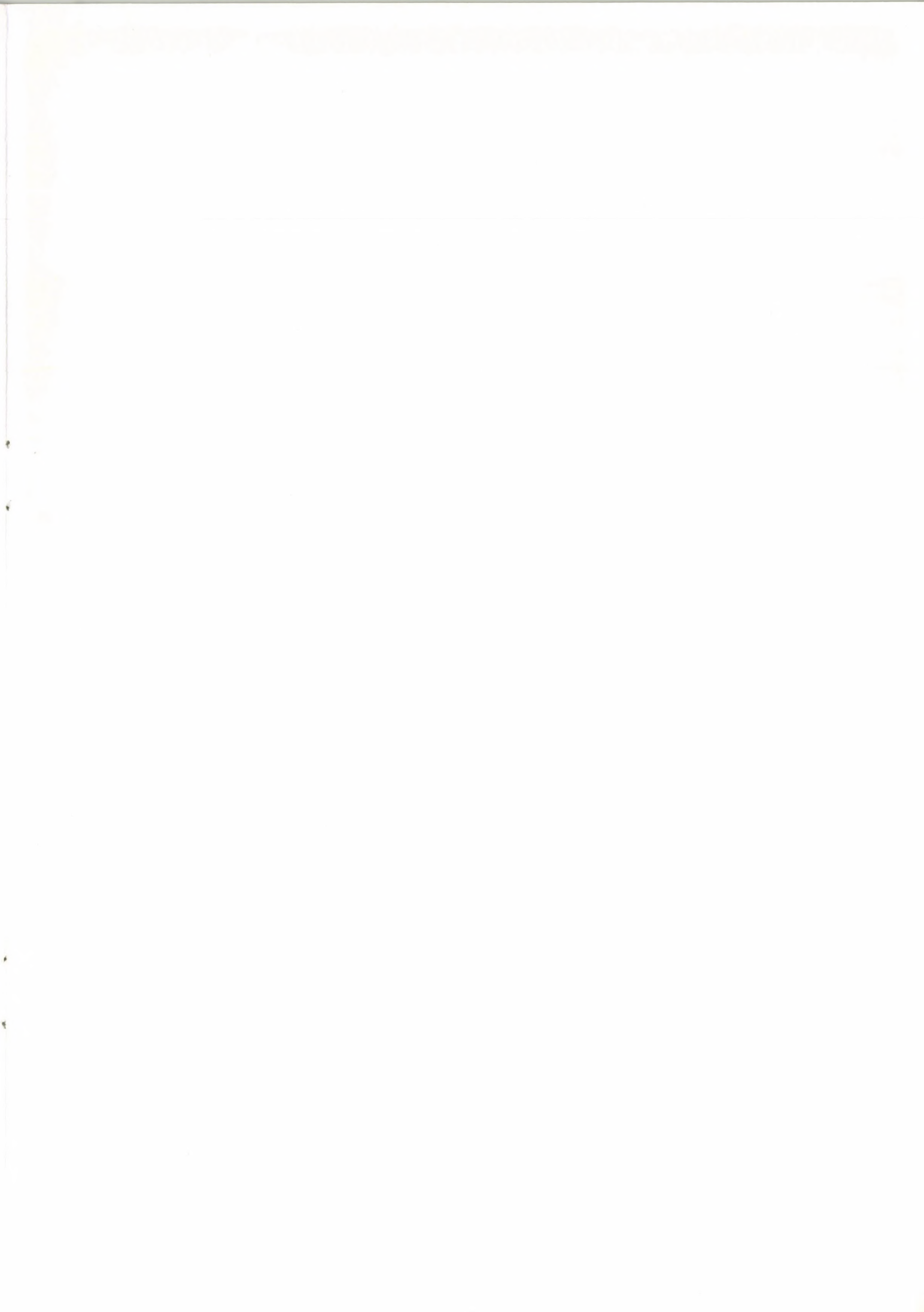


Fig. 9. Dependence of j^x and j' on electrode potential. Data of j' are computed using data of j^x /see present figure $c_{\text{red}}^{\rightarrow\infty}$ / and k_p/k_i /see Fig. 5/. For conditions see Fig. 5.





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